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This is a presentation for the the SAMPE High Desert Conference, about high temperature composite resins and re-writing the rules for thermosetting polymers.

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HIGH-TEMPERATURE COMPOSITE RESINS: RE-WRITING THE RULES FOR THERMOSETTING POLYMERS

20 September 2011

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Outline

- Unusual Structure-Property Relationships in High-T_g Thermosetting Polymers
  - Cause: expansion of the diBenedetto envelope
  - Effects:
    - T_g Significantly above cure temperature
    - “Negative” shrinkage
    - More cross-links = less brittle but easier to permeate
    - Flexible chemical bonds leads to higher T_g
- Implications for Composite Resin Development

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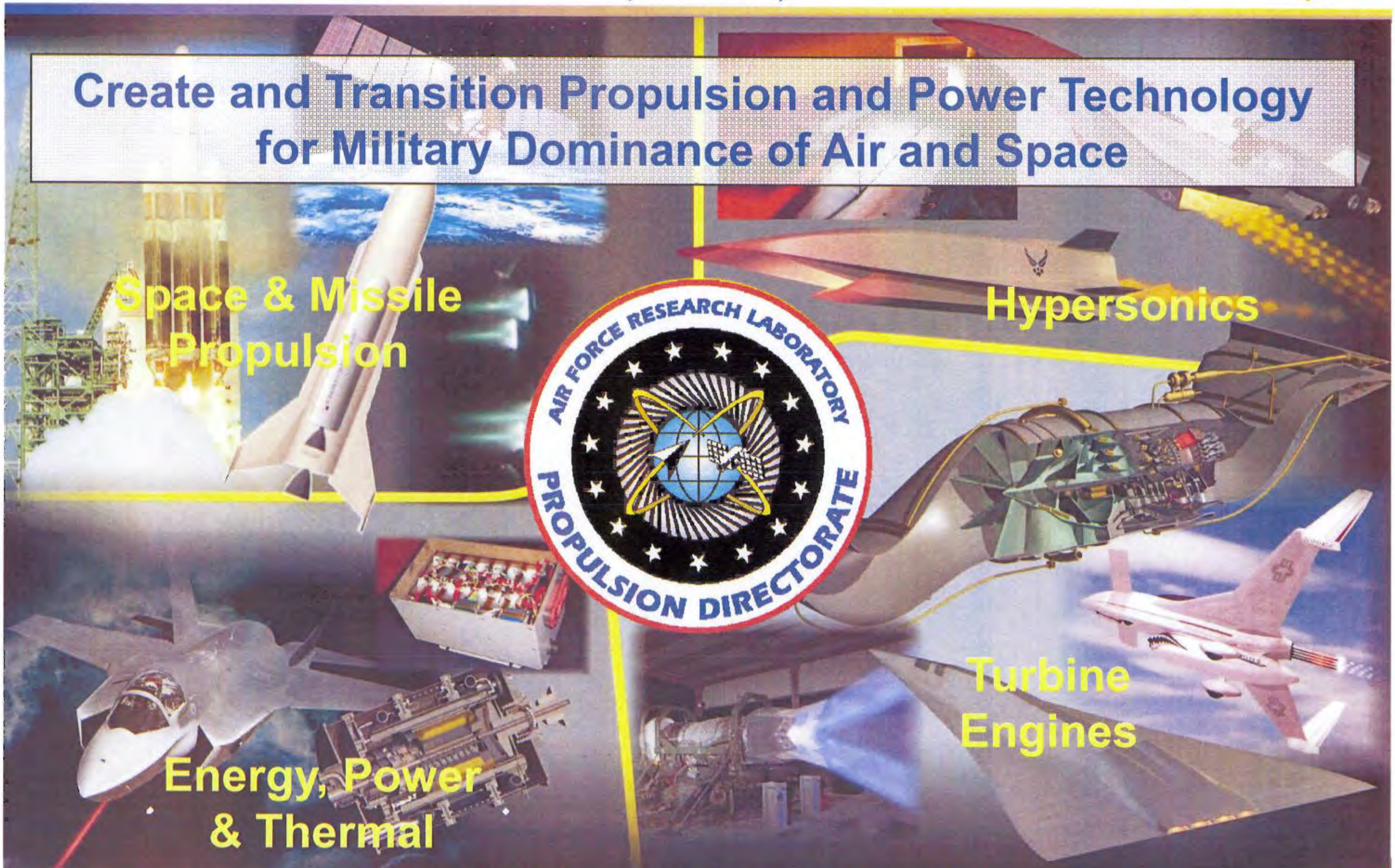

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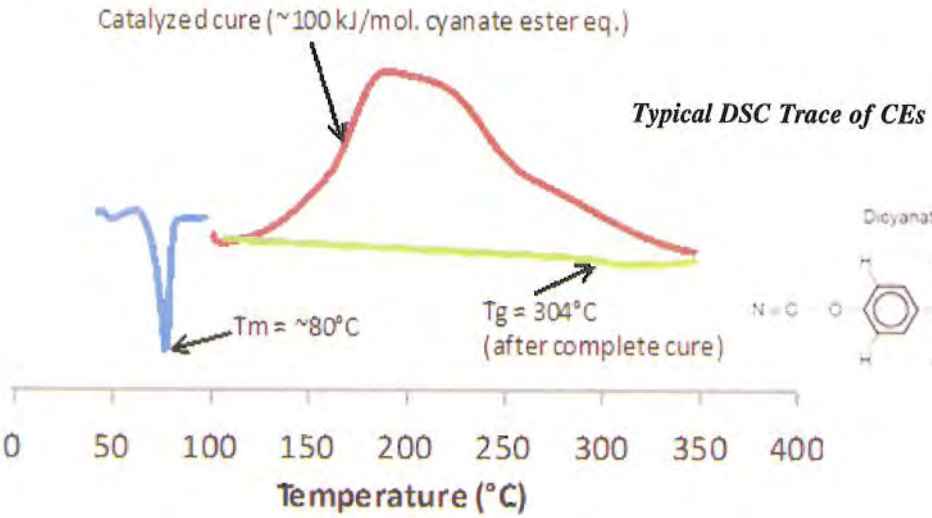
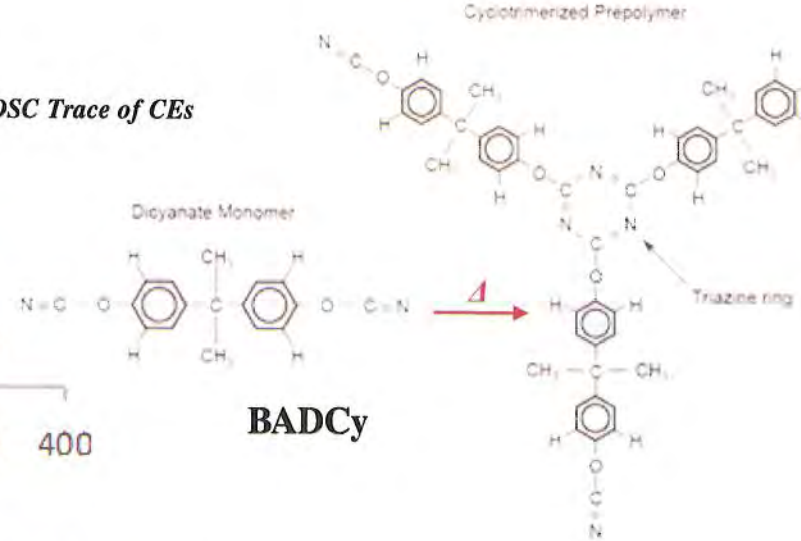
Model High-Temperature Thermosetting Polymers: Cyanate Esters

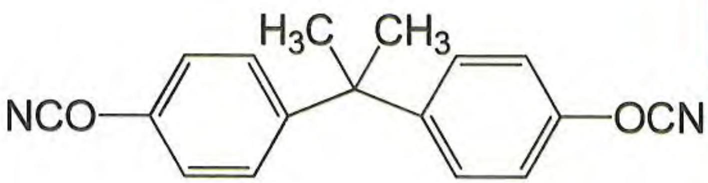




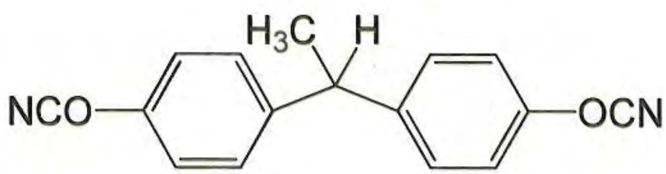
BADCy

- Glass transition temperatures at full cure of 200 – 400°C
- Uncured resins exist as low-melting solids, or low to moderate viscosity liquids, making them ideal for processes such as filament winding
- Broad compatibility with co-monomers, thermoplastic tougheners, or nanoparticles for control of physical and mechanical characteristics
- Single species reaction chemistry is “cleaner” than epoxy resin and well-understood; enables development of superior predictive models for failure; readily catalyzed to cure at reasonable temperatures

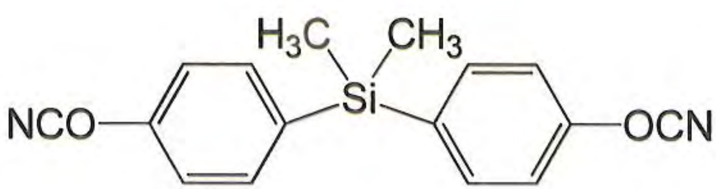
Examples of Cyanate Ester Resins



"BADCy"



"LECy"



"SiMCy"

Name	T_{g0}(°C)*	$T_{g\infty}$ (°C)*	Density* (g/ccl)	Water Uptake*
BADCy	-38	304	1.195	2.3%
LECy	-47	290	1.220	2.4%
SiMCy	-46	260	1.175	1.8%

***after full cure w/ primary cure at 210 °C, systems include catalyst with 160 ppm Cu(II) as Cu(II)AcAc with 2 phr nonylphenol**

- BADCy was the first-commercialized cyanate ester; it is least expensive and has the largest property database
- LECy is the most common room-temperature liquid dicyanate ester often used in filament winding formulations
- SiMCy is a highly useful BADCy analog first synthesized by Wright *et al.* (*Polym. Prepr.* **2004**, *45* (2), 294) noted for its low water uptake

Cyanate Esters: Universe of Applications

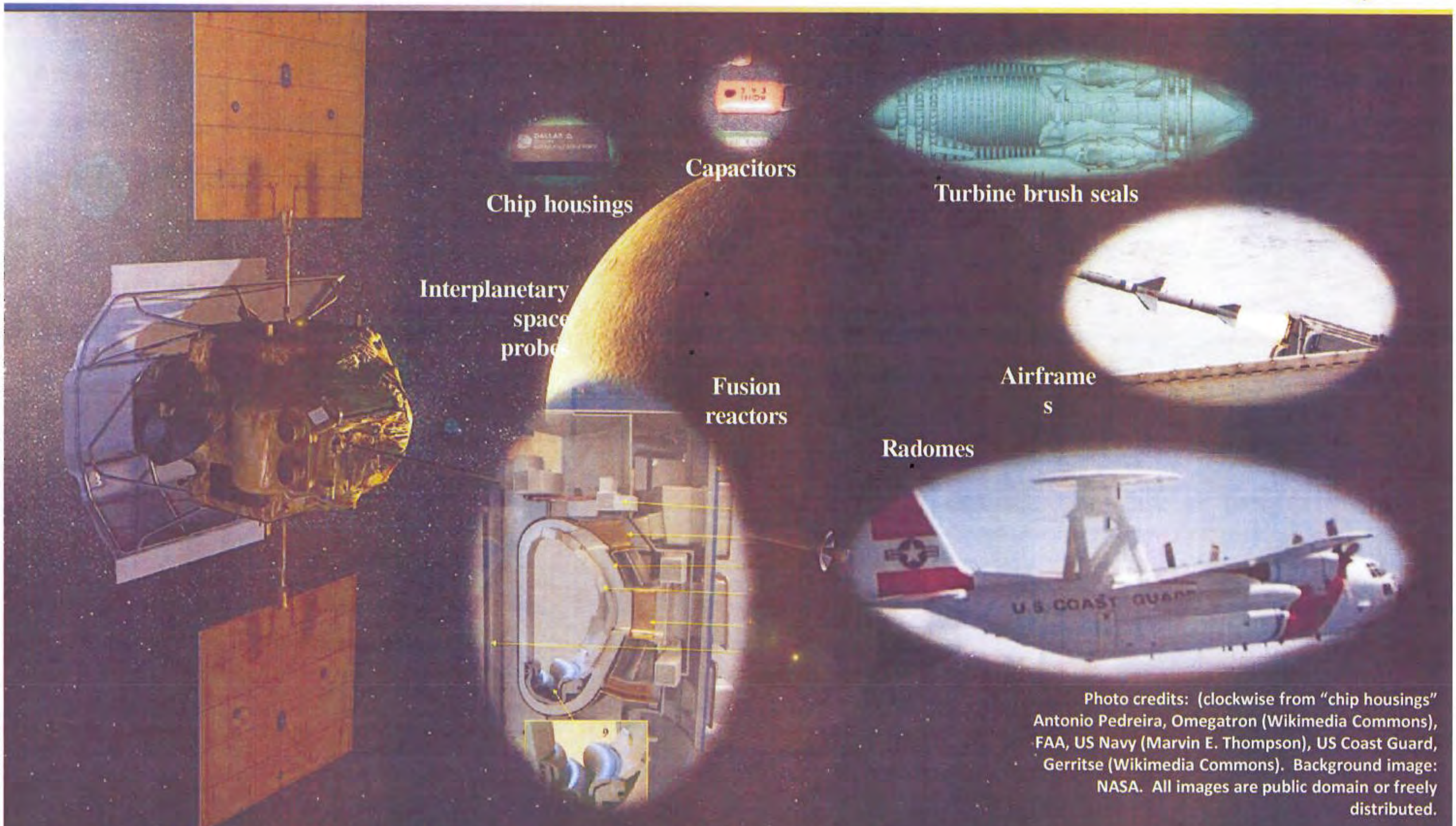
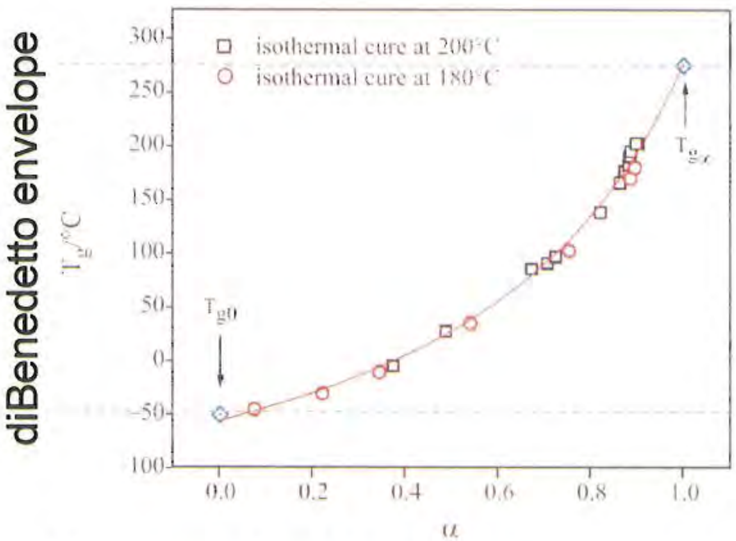


Photo credits: (clockwise from "chip housings" Antonio Pedreira, Omegatron (Wikimedia Commons), FAA, US Navy (Marvin E. Thompson), US Coast Guard, Gerritse (Wikimedia Commons). Background image: NASA. All images are public domain or freely distributed.

- Many opportunities for technical transition …

Glass Transition as a Function of Extent of Cure in a Thermosetting Polymer

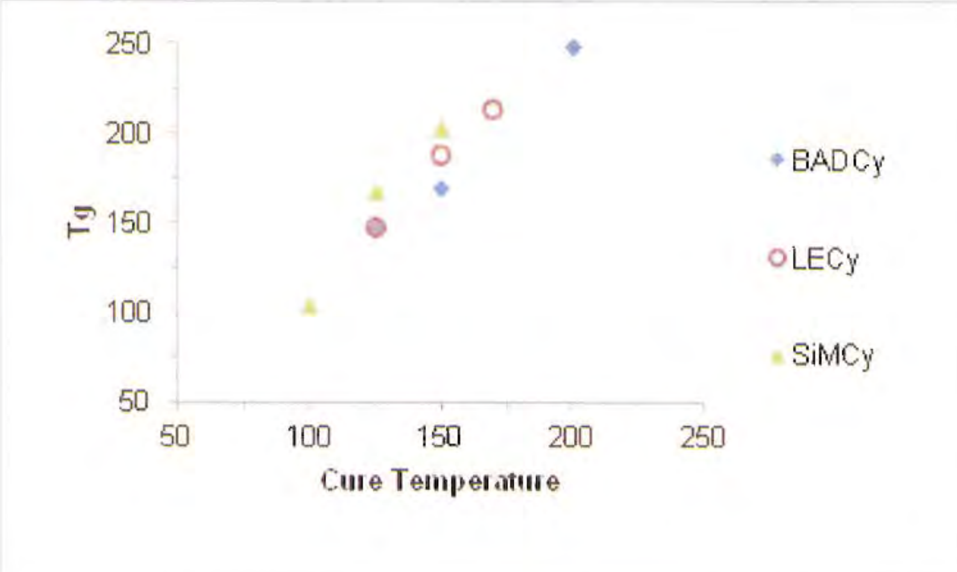


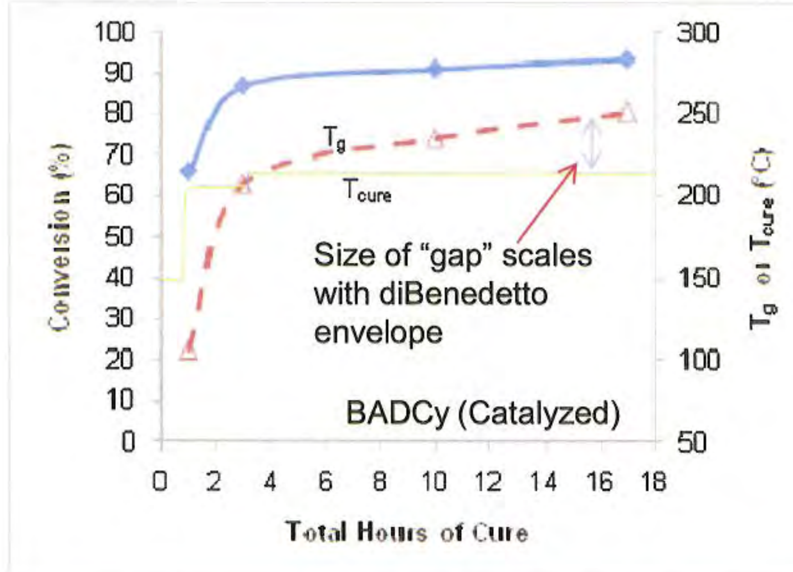
An example of how T_g values can be converted to conversion values based on the diBenedetto equation (from X. Sheng, M. Akinc, and M. R. Kessler, *J. Therm. Anal. Calorim.* **2008**, 93, 77-85.) for EX-1510 dicyanate ester resin, for which $T_g << T_{decomp}$

- Note the steep dependence of T_g on conversion as the system reaches full cure
- The need for higher use temperatures pushes up $T_{g\infty}$ as better performing resins are developed
- The need for ease of processing dictates that T_{g0} remain low, preferably below room temperature
- As a result, composite resins are evolving to have an ever steeper diBenedetto curve, which results in a very strong dependence of T_g on conversion.
- Normally, T_g depends on free volume in polymers, but as conversion dependence begins to dominate, the rules for structure-property relationships change

Material °C→	T_{g0}	$T_{g\infty}$	ΔT_g	$dTg/d\alpha\vert_{\alpha=1}$
Epoxy	0	150	150	4.5
Polyimide	200	450	250	7.5
Cyanate Ester	-50	300	350	10.5

When T_g Rises Fast Enough with Conversion, It Exceeds T_{cure} Despite Vitrification





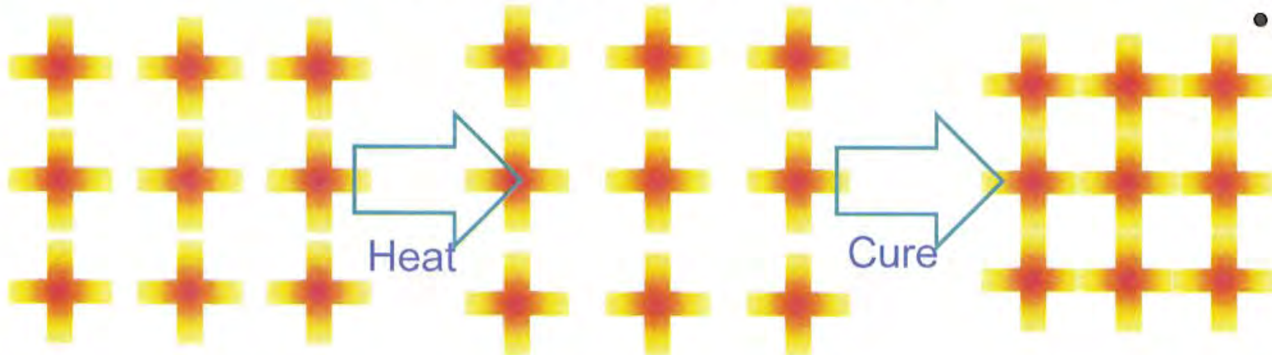
T_g (°C) of Cyanate Esters Cured 12 h

T_{-Cure} (°C)	125	150	170	200
BADCy	134	168	--	246
LECy	142	183	213	--
SiMCy	152	186	--	--

- Vitrification slows down conversion, but does not stop it completely
- Under isothermal conditions, the rate of conversion will fall as conversion increases, but the sensitivity of T_g to conversion will rise, resulting in a fairly constant rise in T_g
- The greater the sensitivity, the further T_g can rise above T_{cure}

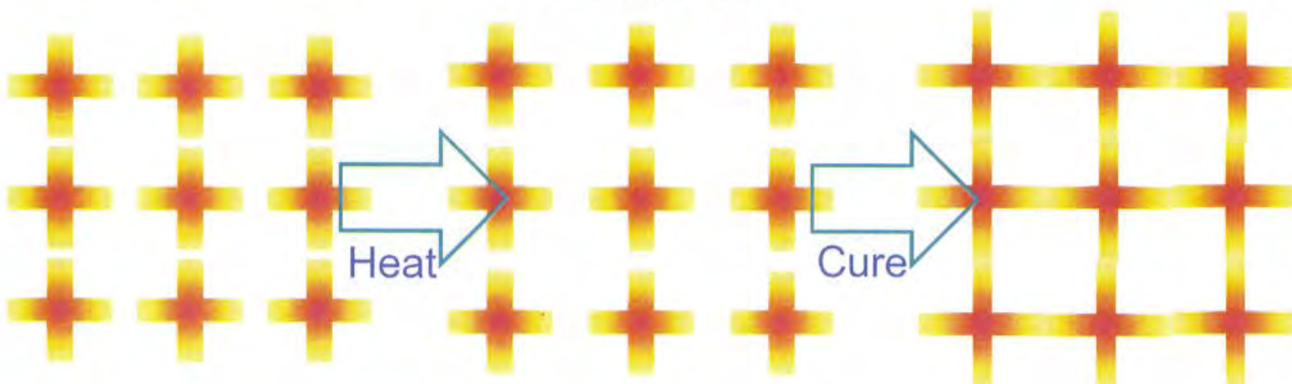
“Vitreous Cure” Changes the Rules of Network Formation

Traditional Thermal Cure



- Cure results in:
  - *Net Shrinkage*
  - *Less permeability*
  - *Higher modulus*
  - *Brittleness*

“Vitreous Cure”



- Cure results in:
  - *Net Expansion*
  - *Higher permeability*
  - *Lower modulus*
  - *Toughness*

- “Vitreous Cure” is promoted by rigid network segments with well-distributed extensibility, and by cure temperatures that are low in comparison to T_g (though $T_{cure} < T_g$ may not be a criterion)
- Both types of cure can happen sequentially, simultaneously, or in mixed form

Evidence for "Vitreous Cure" in Cyanate Esters

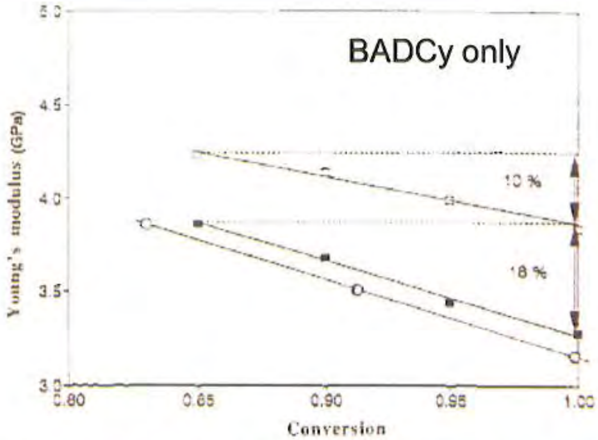
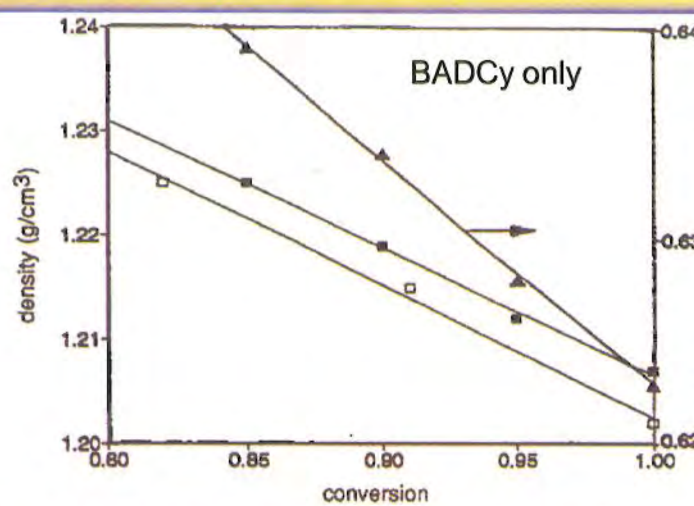


Figure 2 Variation of the (■) Young's modulus and (□) ultrasonic modulus as a function of conversion (uncatalyzed networks). (○) Variation of the Young's modulus of catalyzed networks.



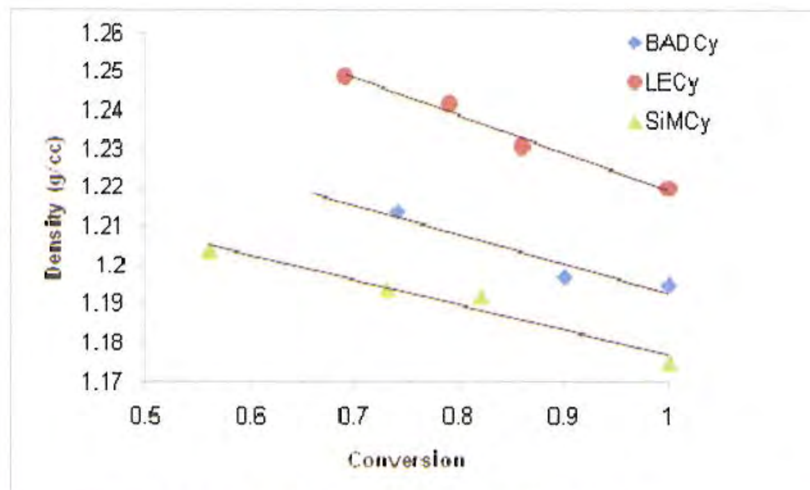
Georjon, O. and Galy, J. *Polymer* 1998, 39, 343

Figure 3 Density values as a function of conversion (at room temperature): ■, uncatalysed networks; □, catalyzed networks; ▲, packing density of uncatalysed networks

Georjon O and Galy J. *Journal of Applied Polymer Science 1997;65(12):2471-2479.*

Table V Values of Stress Intensity Factor K_{IC} and Fracture Toughness G_{IC} for Different Polycyanurate Networks BADCy only

Network	K_{IC} (MPa $\sqrt{m}$)	G_{IC} (J/m^2)
100	0.8	170
95	0.5	60
90	0.5	55
85	0.3	20
C100	0.9	220
C91	0.6	90
C82	0.4	35



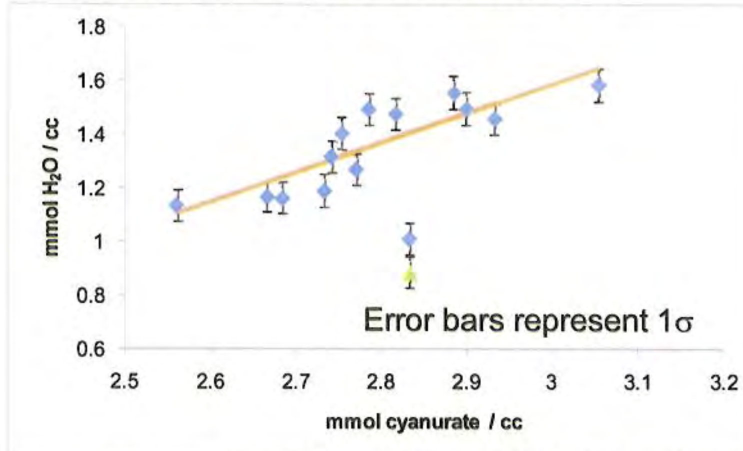
… as confirmed by recent AFRL data

Correlation Between Water Uptake, and Cyanurate Density

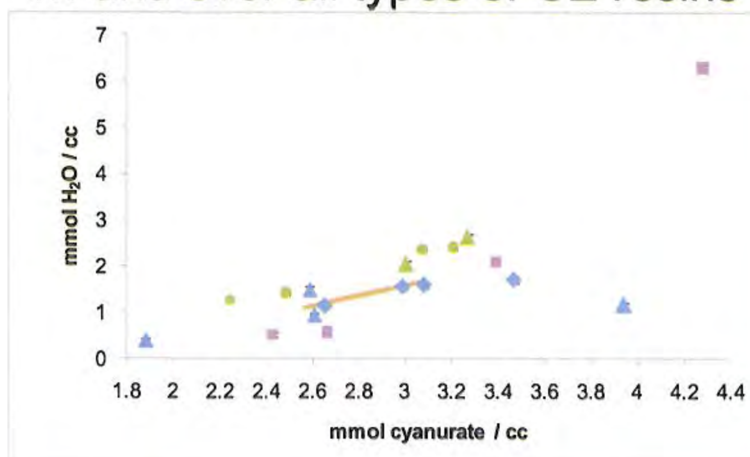
Cyanate Ester - mmol cyanurate/ cc	mmol H_2O / cc
BADCY /3.0	1.7
LECY/ 3.0	1.6
SIMCY / 2.7	1.1
THIOCY / 3.9	1.2
METHYLCY / 2.6	0.9
AroCy F / 2.6	1.5
REX-371 / 3.3	2.6
RTX366 / 1.9	0.4

•Based on data in Appendix a-3 of Hamerton, I (ed)., Chemistry and Technology of Cyanate Ester Resins (Blackie Academic, 1994) (uses monomer density)

In blend samples studied …



… and over all types of CE resins …

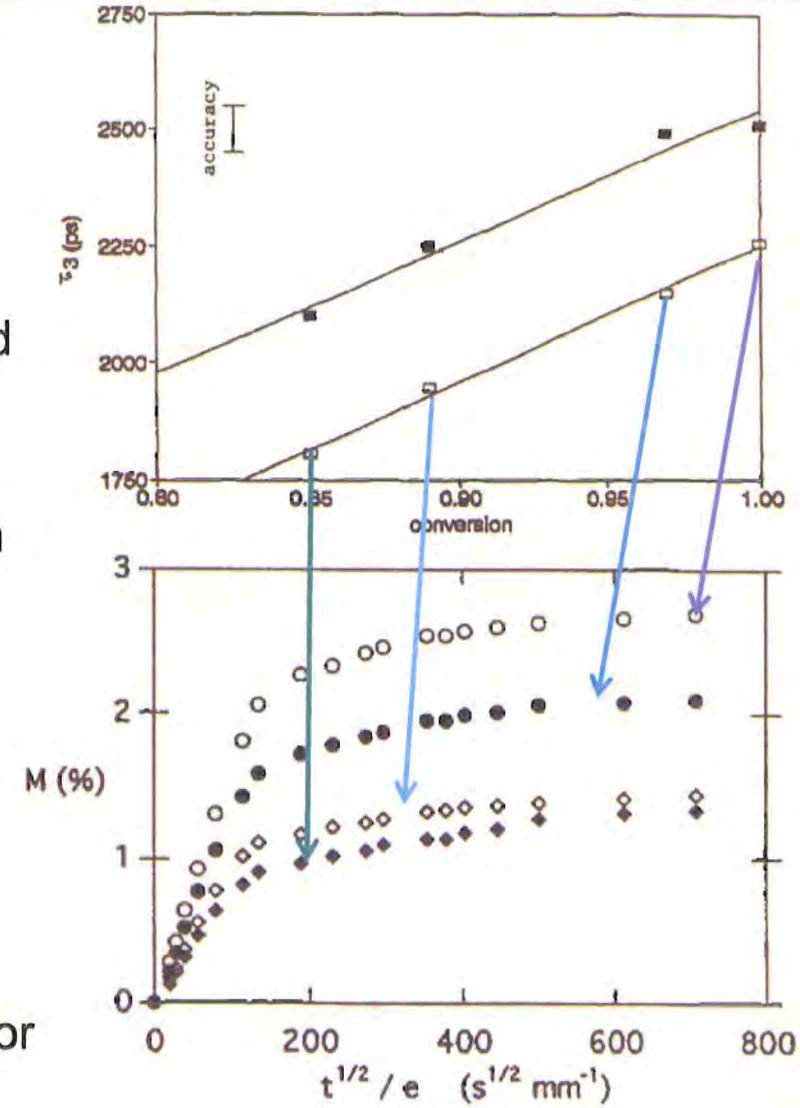


Blue = bisphenyl
Green = three-arm
Purple = single-ring (meta)
Orange = blend data
Triangle = lit. value (x-axis uncertain)

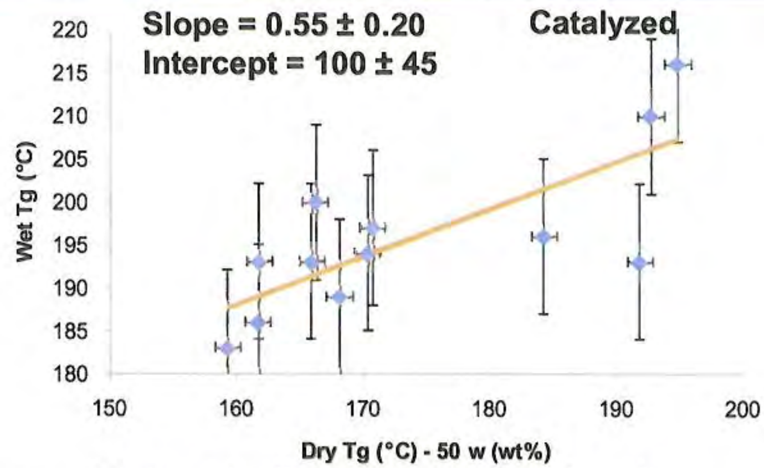
- Maintaining a low density of cyanurate groups appears to limit water uptake

Water Uptake and Free Volume Associated with Cyanurate Groups

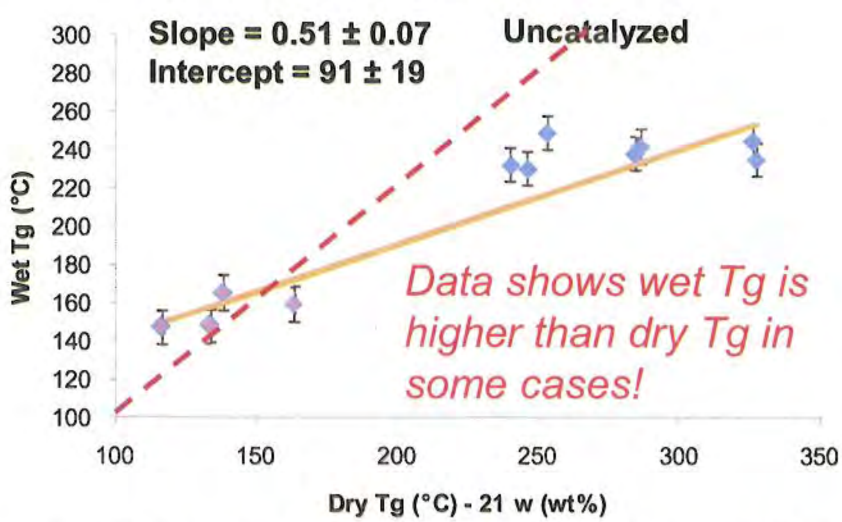
- Georjon and Galy (Polymer 39, 343, 1998) showed that, for BADCy, the late stages of cure led to an increase in free volume associated with the formation of cyanurate groups, and that the formation of free volume was directly connected to increased water uptake.
- Our results to date show:
  - A similar correlation at high conversion for other dicyanate monomers
  - That the effect is limited to very high conversions (otherwise both water uptake and free volume decrease with increasing conversion), and
  - Monomers with more free volume overall tend to absorb less water
- Thus, all free volume is not equally useful for water uptake.



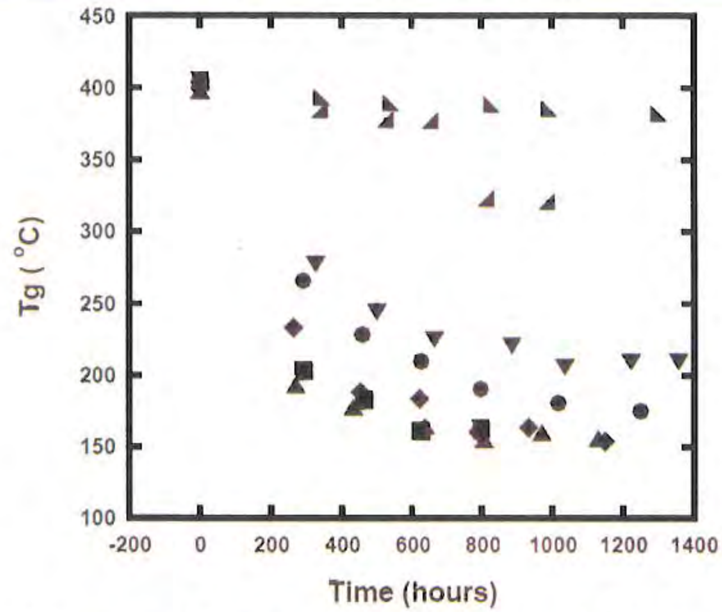
Quantitative Prediction Tools for Wet T_g



- From studies of ternary blends



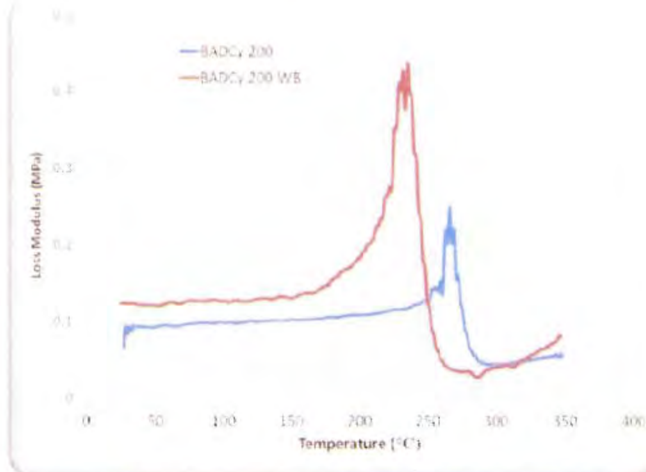
- And from studies of molecular architecture

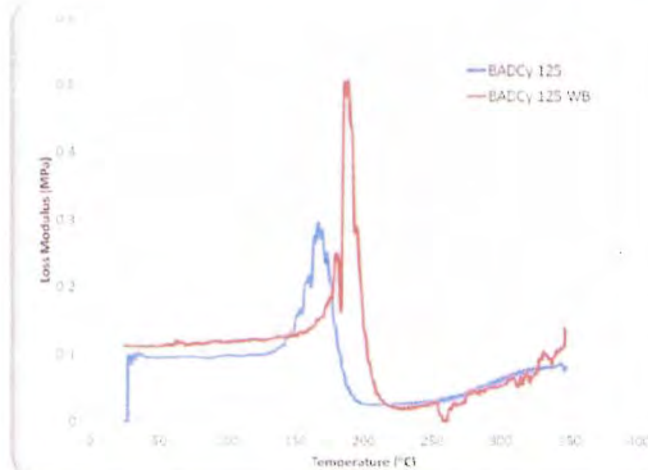


- Marella (thesis, Drexel Univ., 2008) showed that uncatalyzed PT-30 cyanate ester exhibits only about 65% of the drop in Tg compared to a mildly catalyzed system; our measurement of the same effect yields a ratio of 40 ± 25%.

Comparison of Wet and Dry T_g in Partially Cured Dicyanates

Sample ID	Dry T_g (°C)	Wet T_g (°C)
BADCy 125	147	171
BADCy 150	169	190
BADCy 200	248	220
LECy 125	147	170
LECy 150	188	187
LECy 170	213	192
SiMCy 100	105	136
SiMCy 125	168	162
SiMCy 150	203	179





- Hot/wet exposure can increase T_g in common dicyanates too.

The Role of Flexible Junctions in Cyanate Ester Networks

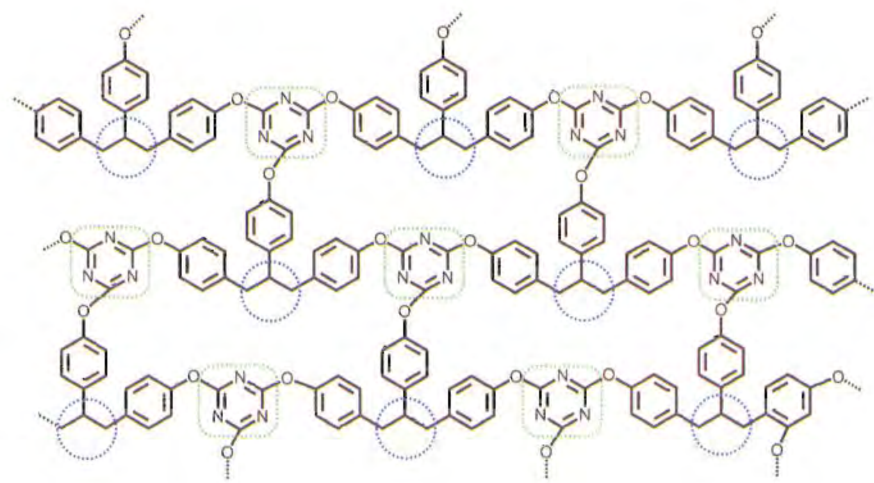
GOAL: Replace cyanurate linkages with alternative network linkages to generate high Tg values via a high density of cross-linked network junctions without increasing water uptake, and while preserving toughness.

"FlexCy"

AF/Navy Collaboration:

Monomer synthesized by Dr. Matthew Davis at NAWCWD China Lake

NAVAIR



Publications:

Guenthner, A. J.; Davis, M. C.; Lamison, K. R.; Yandek, G. R.; Cambrea, L. R.; Groshens, T. J.; Baldwin, L. C.; Mabry, J. M. "Synthesis, Cure Kinetics, and Physical Properties of a New Tricyanate Ester with Enhanced Molecular Flexibility", *Polymer*, 2011, 52, 3933-3942

; see also, same authors, "Cure Characteristics of Tricyanate Ester High-Temperature Composite Resins" in *Proceedings of SAMPE '11*.

Conversion Measurements for FlexCy and PT-30

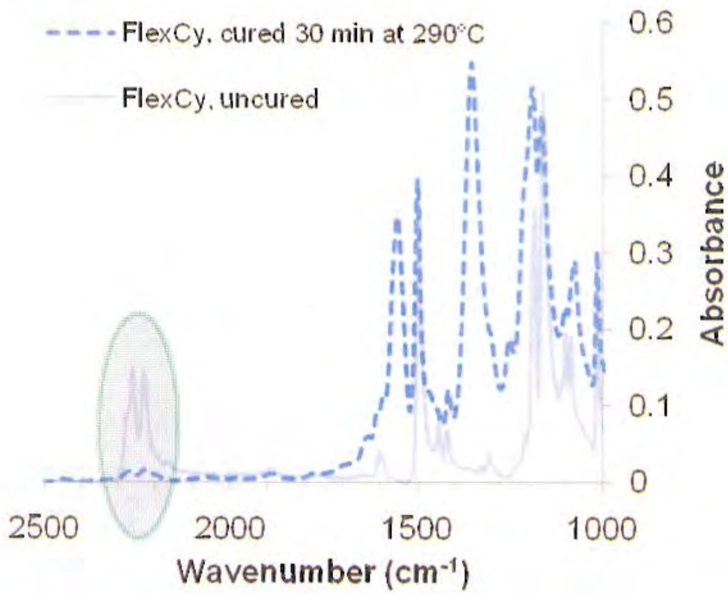
Material	Cure Temp. (°C)	Cure Time (hrs)	Tg via OTMA CTE (°C)	Tg via OTMA Loss Peak (°C)	Conversion via OTMA CTE	Conversion via OTMA Loss Peak	Conversion via FT-IR	Conversion via DSC
FlexCy-IPA	210	24	310	338	0.91	0.92	0.83	n/a
FlexCy-IPA	250	2	307	>352[a]	0.90	>0.94	0.82	n/a
FlexCy-IPA	290	0.5	>349[a]	>349[a]	>0.95	>0.94	0.94	<0.98
FlexCy-IPA[c]	210 / 290	24 / 0.5	302	351	0.89	0.94	n/a	n/a
FlexCy-EtOH	210	24	301	317	0.89	0.88	n/a	n/a
FlexCy-EtOH	250	2	327	>354[a]	0.93	>0.94	n/a	n/a
FlexCy-EtOH	290	0.5	301	>352[a]	0.89	>0.94	n/a	<0.98
PT-30	210	24	274	309	0.82	0.85	0.80	n/a
PT-30	250	2	309	>355[a]	0.88	>0.93	0.91	n/a
PT-30	290	0.5	327	>352[a]	0.91	>0.92	0.80	<0.99
PT-30[c]	210 / 290	24 / 0.5	314	>389[a]	0.89	>0.98	n/a	n/a

a. Run terminated due to sample decomposition prior to measurement of loss peak

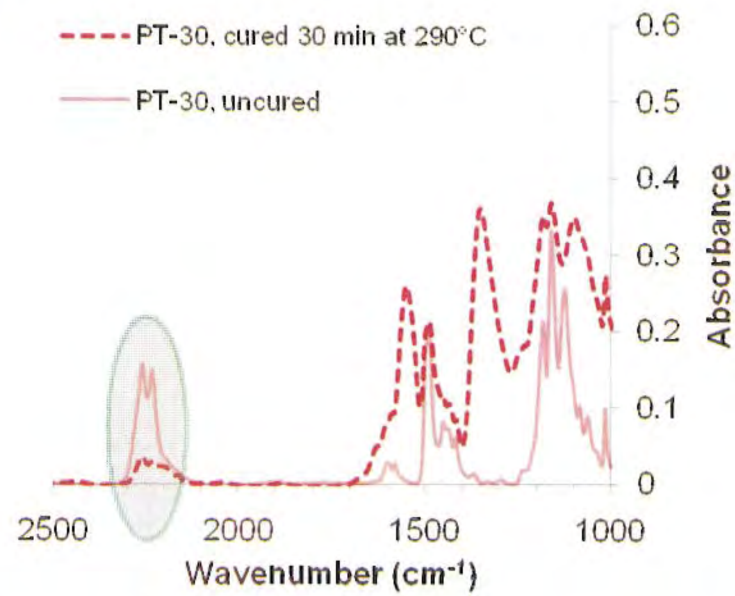
- Under some cure conditions, FlexCy exhibits a higher T_g than PT-30, indicating a higher extent of cure was achieved
- Although all samples show >80% conversion, quantitative comparisons are difficult

FlexCy and Primaset® PT-30: FT-IR Cure Comparison

FlexCy



PT-30



- FT-IR conversion estimates of 95% (FlexCy) and 80% (PT-30) are only approximate but show clearly that incorporation of the alternative linkage types facilitates full cure of the cyanate ester groups, improving dry T_g and toughness.
- Because of the high sensitivity of T_g to conversion that results from the large diBenedetto envelope, the T_g increase driven by higher conversion can outweigh the expected T_g decrease due to incorporation of flexible chemical bonds.

Summary of Technical Content

- The need for increased high-temperature performance while maintaining affordable processing for polymer matrix composite resins is driving the use of materials with a wider diBenedetto envelope (difference in cured and uncured T_g).
- A wider diBenedetto envelope means that the resin T_g can increase substantially with a very small increase in the extent of cure, which allows the resin T_g to significantly exceed the cure temperature, promoting "vitreous cure".
- Increased "vitreous cure" results in unusual structure-property relationships, including
  - Decreased density with increasing cure
  - Increased toughness with increasing cure
  - Increased water uptake with increasing cure
- Efforts to quantify the effect of cure on wet T_g are underway. There appears to be a correlation between extent of cure and extent of "knockdown" but details (including the reason for unusual increases in T_g on exposure) are not yet clear.
- The high sensitivity of T_g to extent of cure also means that, in some cases, the judicious addition of flexible chemical linkages (that promote extent of cure) can result in a net increase in T_g under some cure conditions.

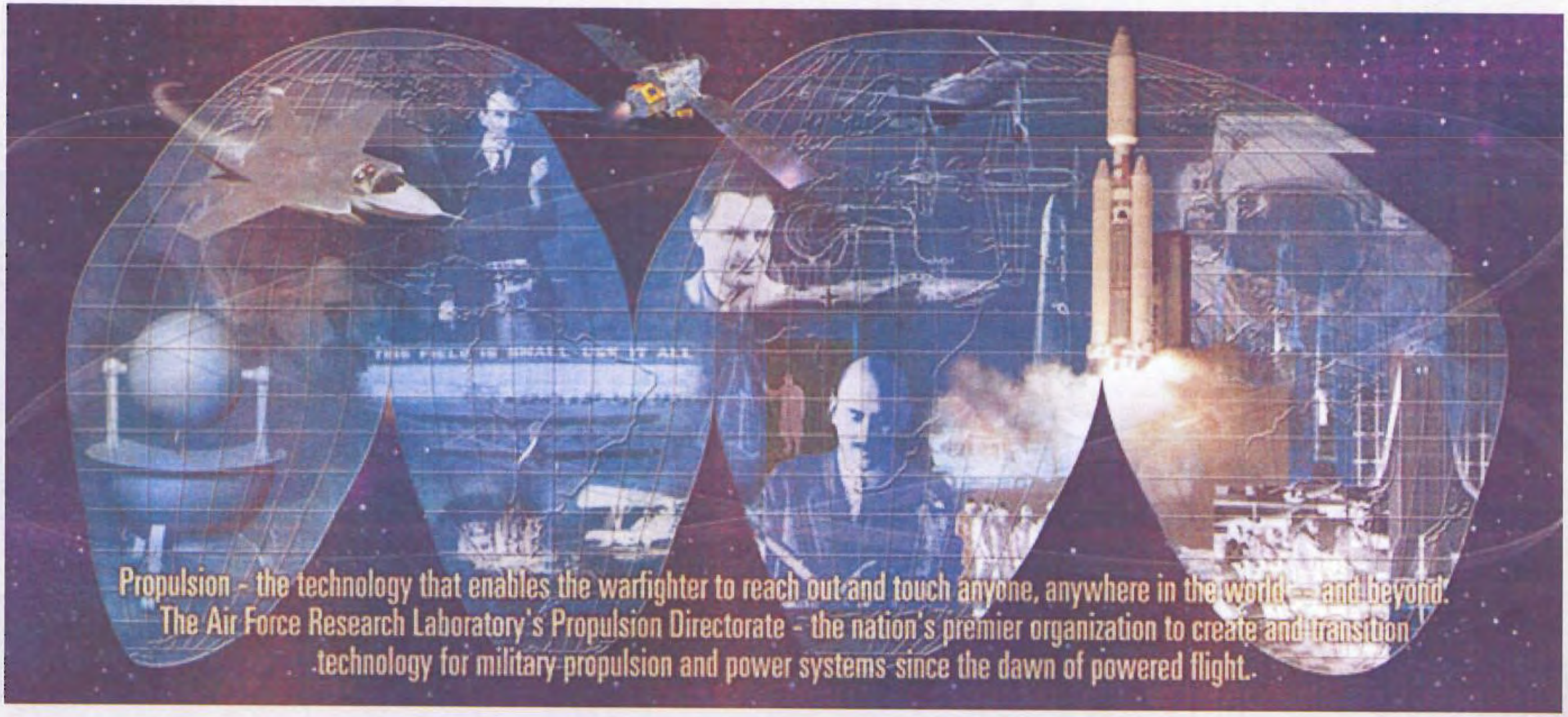
Implications for Composite Resin Development

- Awareness of the Unusual Structure-Property Relationships Helps to …
  - Minimize moisture uptake and improve hot / wet performance in high temperature polymer matrix composites
  - Take advantage of previously unrecognized means of improving resin toughness (near-complete cure and judicious use of flexible bonds) without sacrificing high use temperatures
  - Better understand the impact of cure schedule on physical properties
- Impact for USAF: More Reliable and Better-Performing Rocket / Airframe Propulsion
  - Hot / wet performance is often the limiting performance factor
  - Detection of mechanical damage is the major reliability concern

Atlas V

The Next $50 Billion

- Despite claims that composites represent a "mature" technology, a 30% cost reduction for composites is expected to result in a 200% increase in the size of the market (similar situation for photovoltaics)
  - Growth can be found at both the high end and the low end of performance
  - In 2010, the market for composite products was $50B, but only $17.7B went for materials ($8.8B resin; $7.7B fiber, $1.2B other)
  - If the cost of processing is not also considered, next-generation materials are likely to have a limited impact on achieving market growth
  - One good way to drive out cost is to cut back on over-designing; better general structure-property relationships are an important enabling factor
  - A good set of structure-property relationships is highly reusable and will ultimately cost far less than a good database



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